

THE POWER of VOLTAMMETRY

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Cyclic voltammogram
of hydroxy-ferrocene.



**Alexander von HUMBOLDT KOLLEG
Macedonia 19-23 April
OHRID**

...at the door of EU

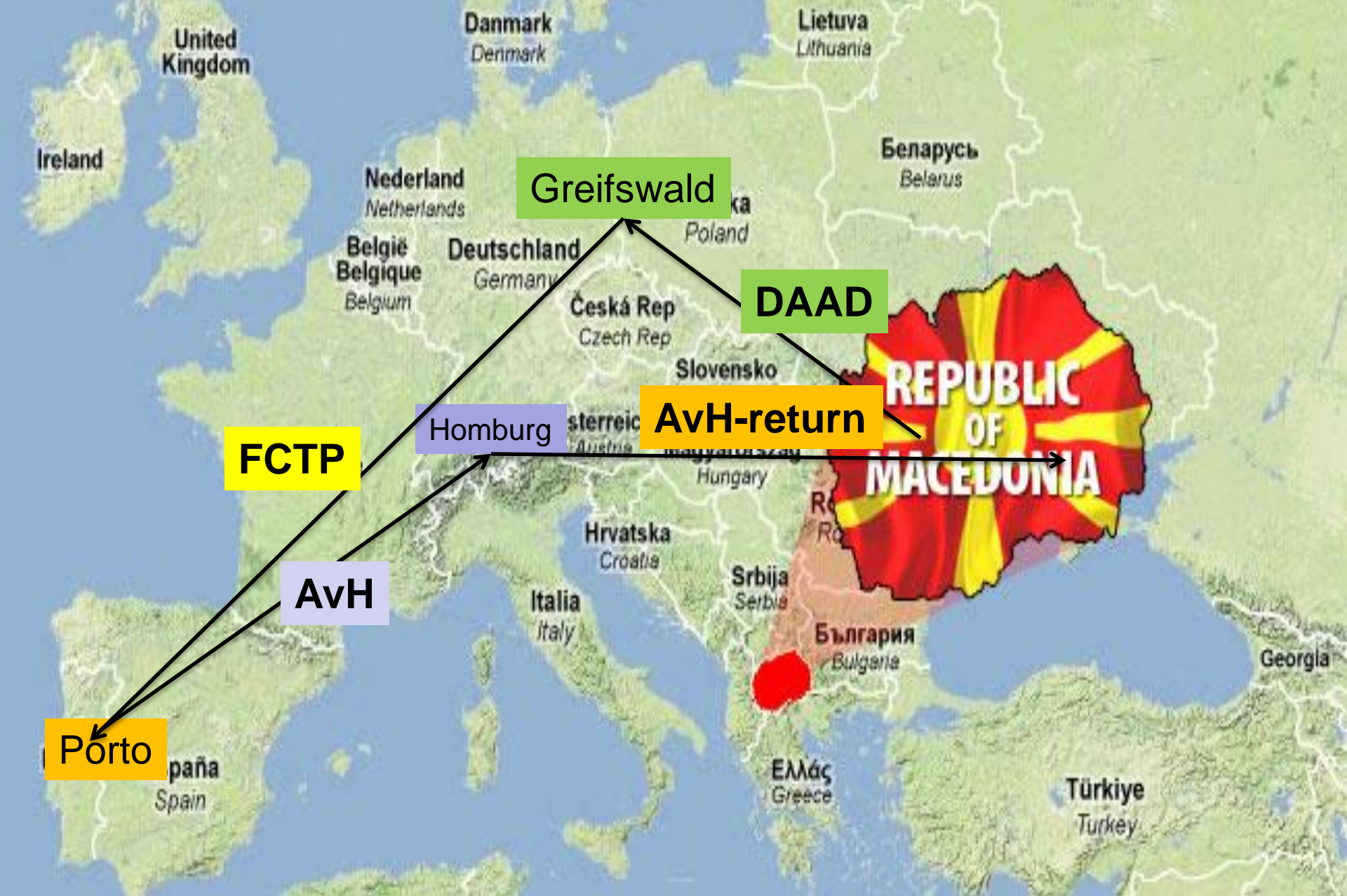


**Goce Delcev
University, Stip
MACEDONIA**

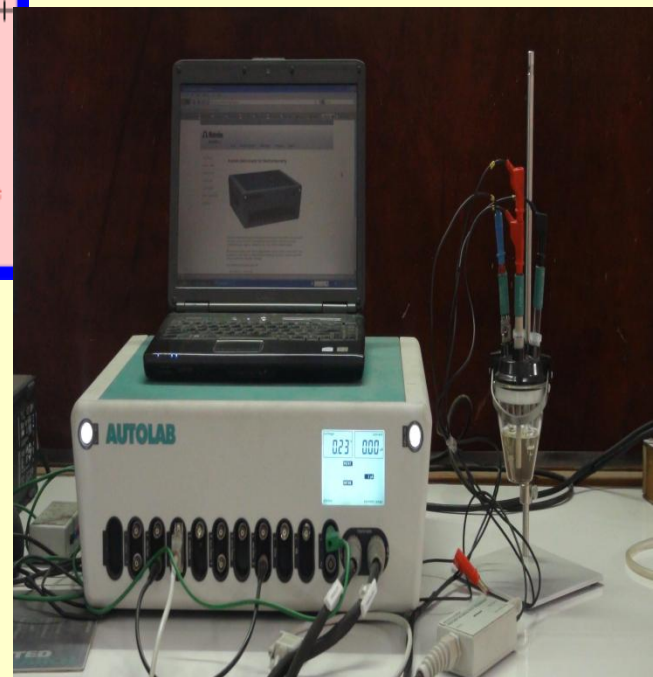
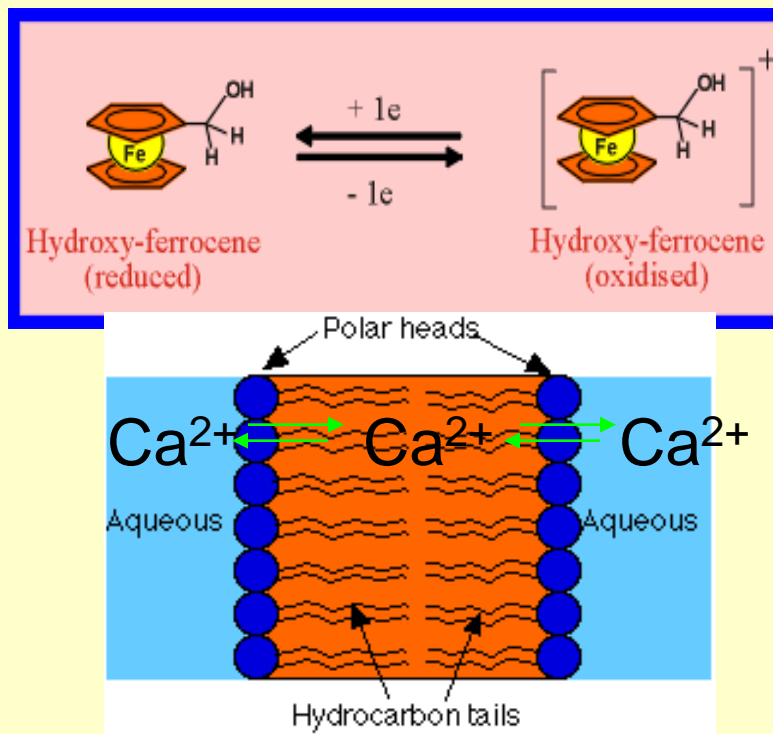




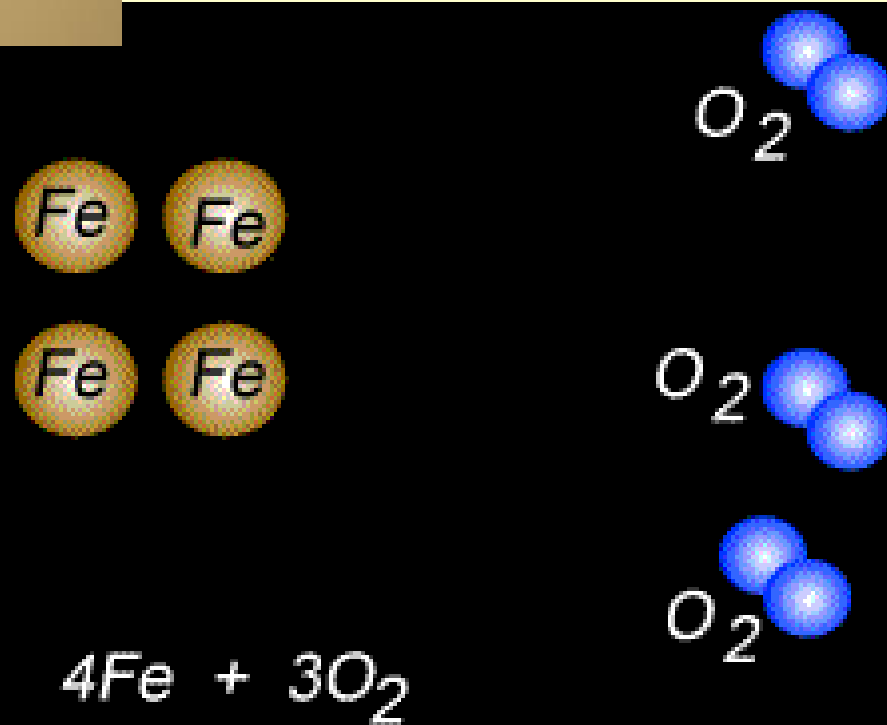
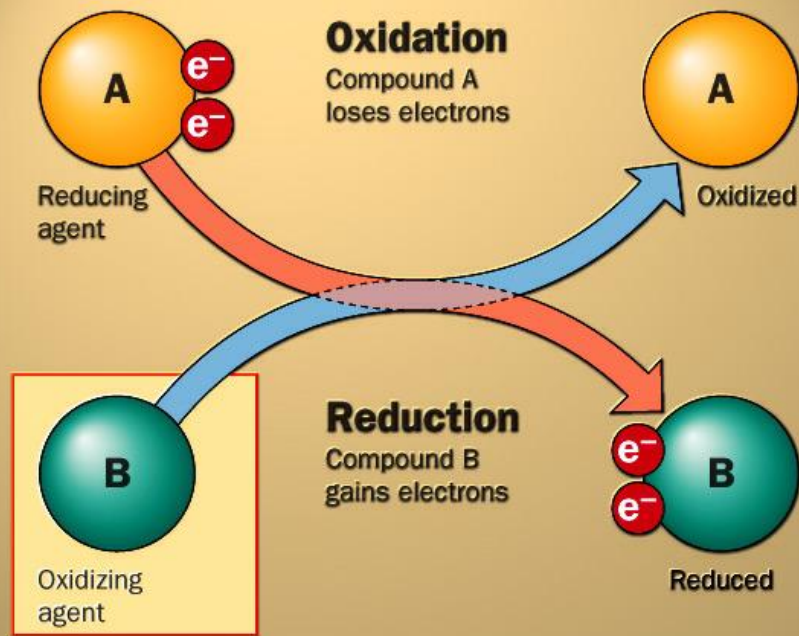
**“HUMBOLDT ALEE” at the
Institute of Chemistry, SKOPJE----why?**



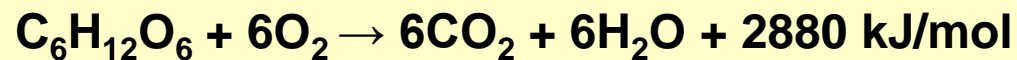
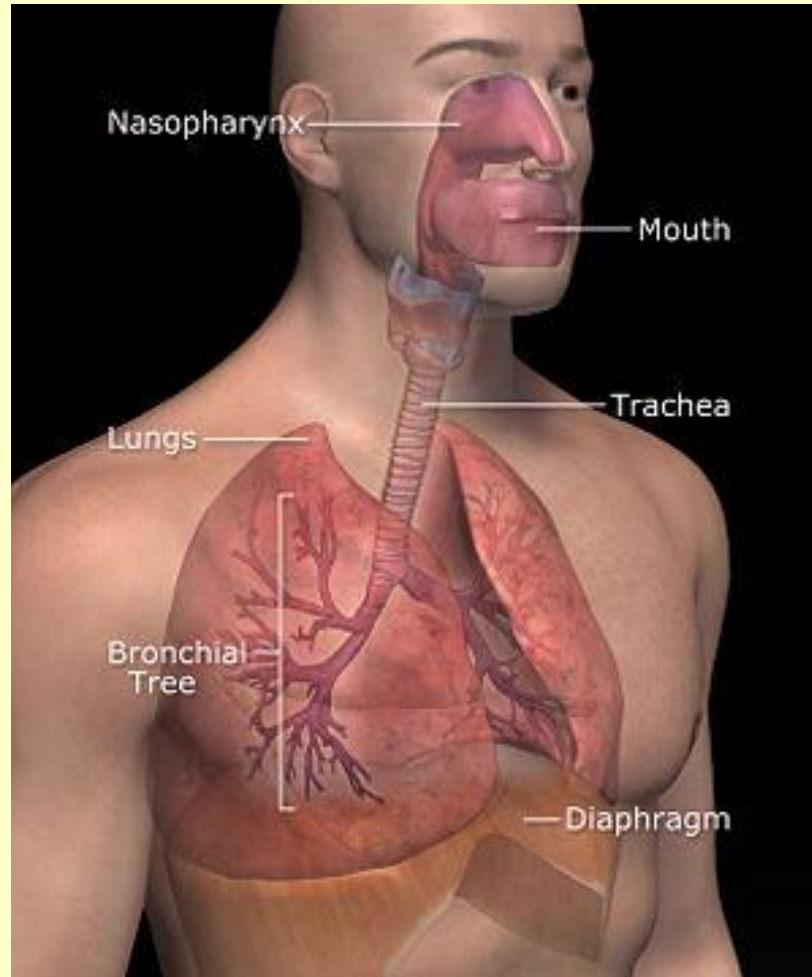
VOLTAMMETRY is a branch of **ELECTROCHEMISTRY**
-deals with the processes of **CHARGE** transfer
between two systems
-**FLOW** of electric charge=**CURRENT**

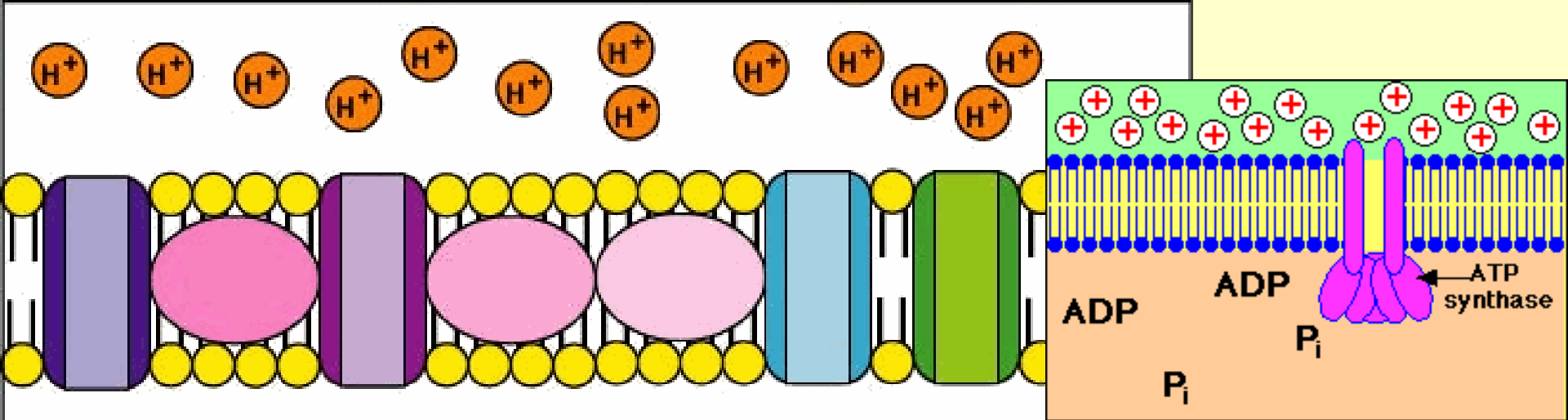


We can say-voltammetry deals MAINLY with Processes of oxidation and reduction

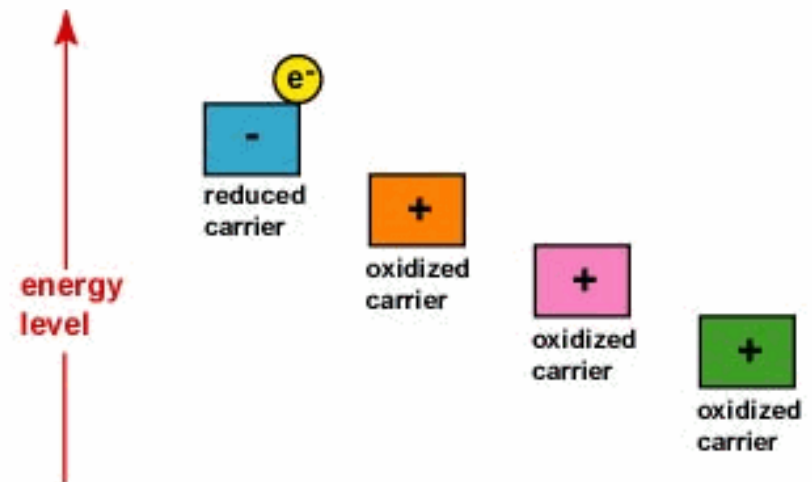


Milions of processes in living Systems have oxidation-reduction nature





**The Electron Transport Chain
CREATION OF ATP**
From FOOD is, indeed
the most important
Electrochemical process
in living systems

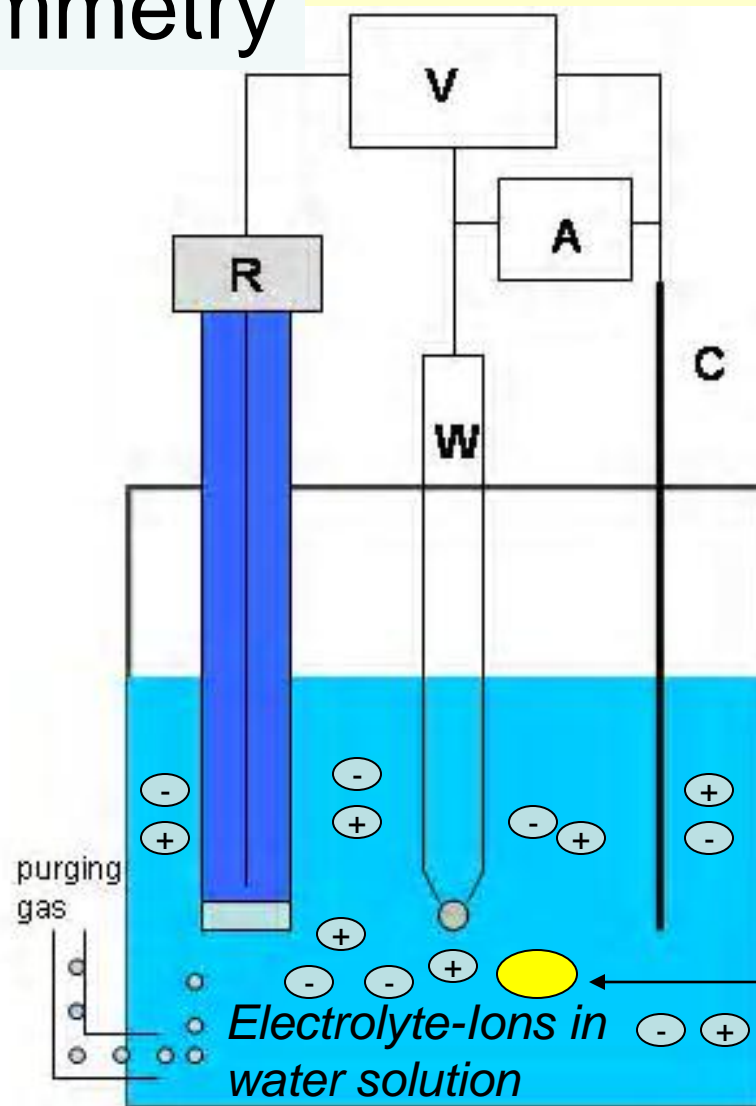


Voltammetry

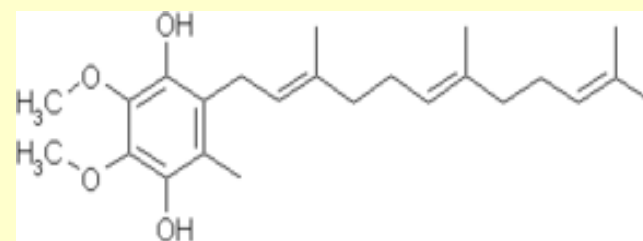
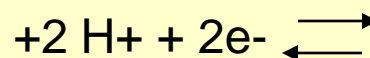
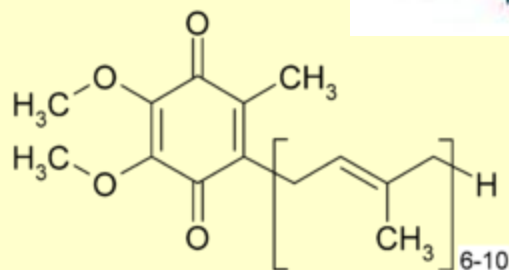
W-working electrode



R-reference electrode



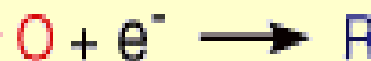
Redox probe



Reactant (O)

Product (R)

Transport of products
and reactants



electrode

e^- e^- e^-

Cyclic voltammogram
of hydroxy-ferrocene.



Application of the Voltammetry

-In Chemistry, Physics and Engineering

-In Biology and Biochemistry
(biosensors)

-In Pharmacy

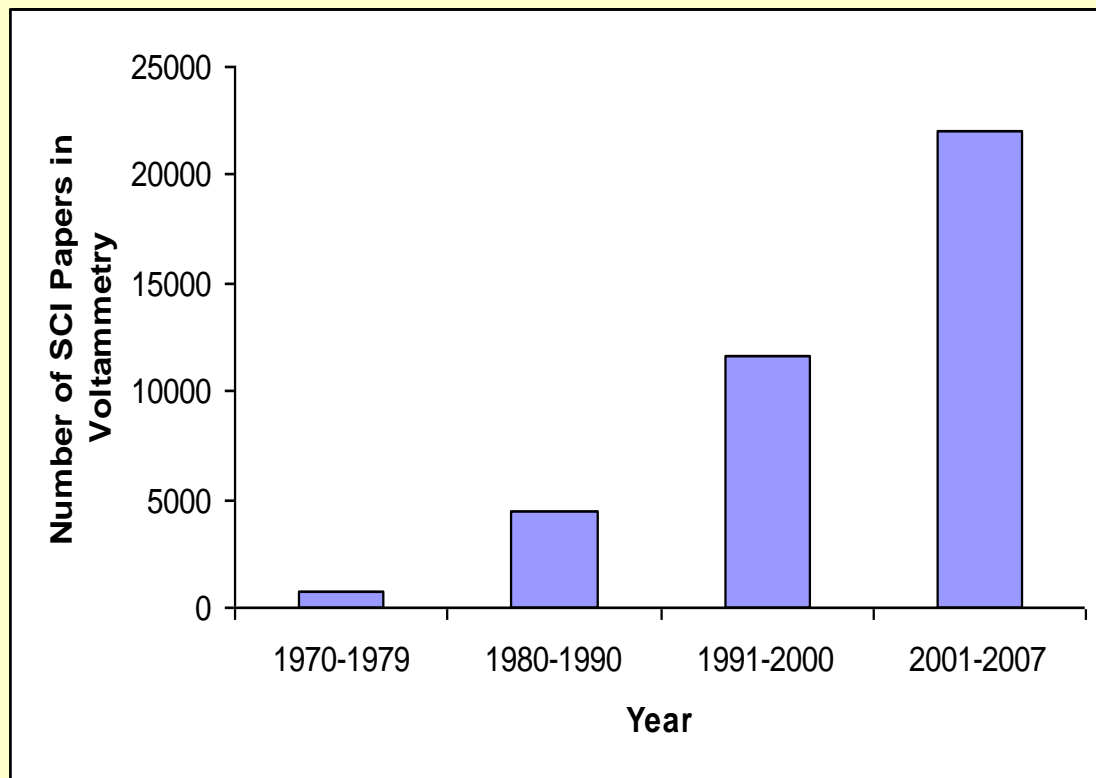
-In Medicine

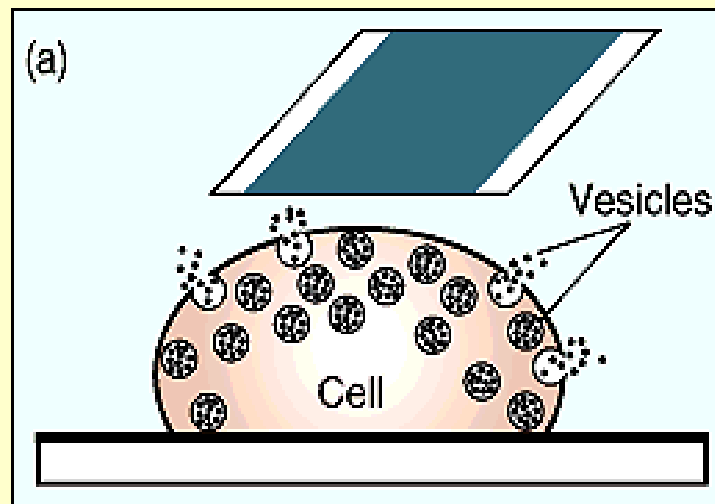
-detection of reactive radicals
nitroxides, superoxides,...

-determination of various
active compounds

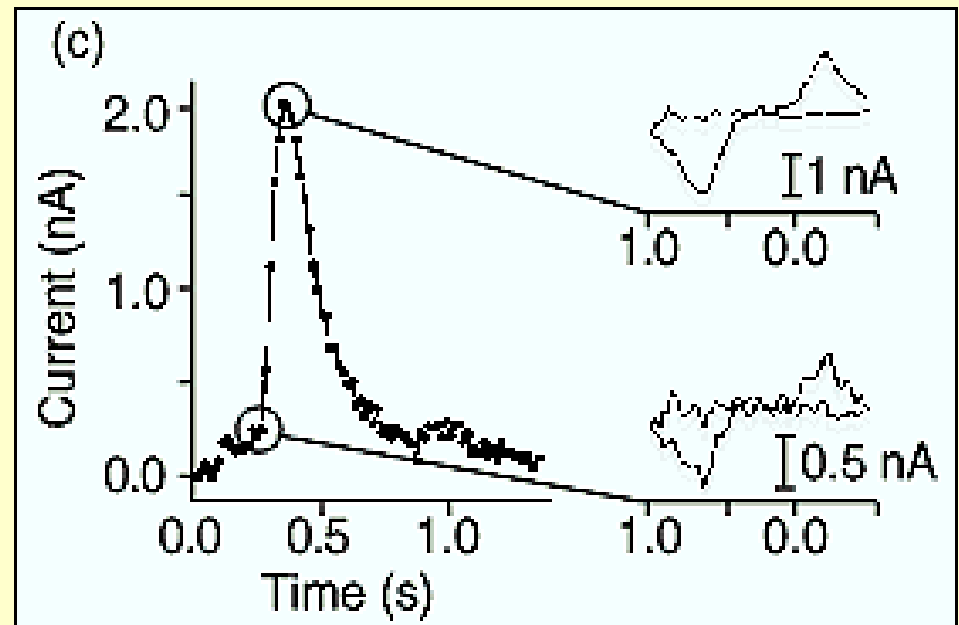
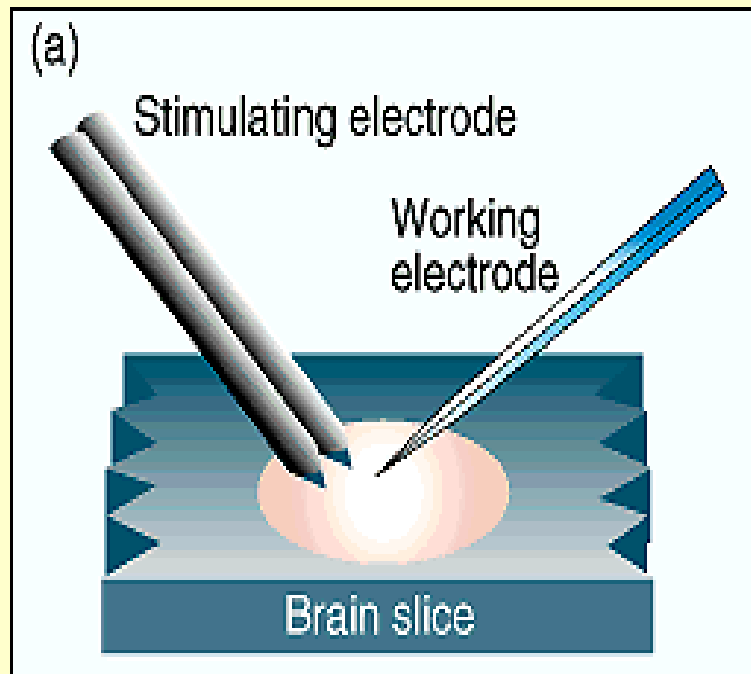
-following of protein-protein interactions

-medical sensors for various
electron carriers and neurotransmitters





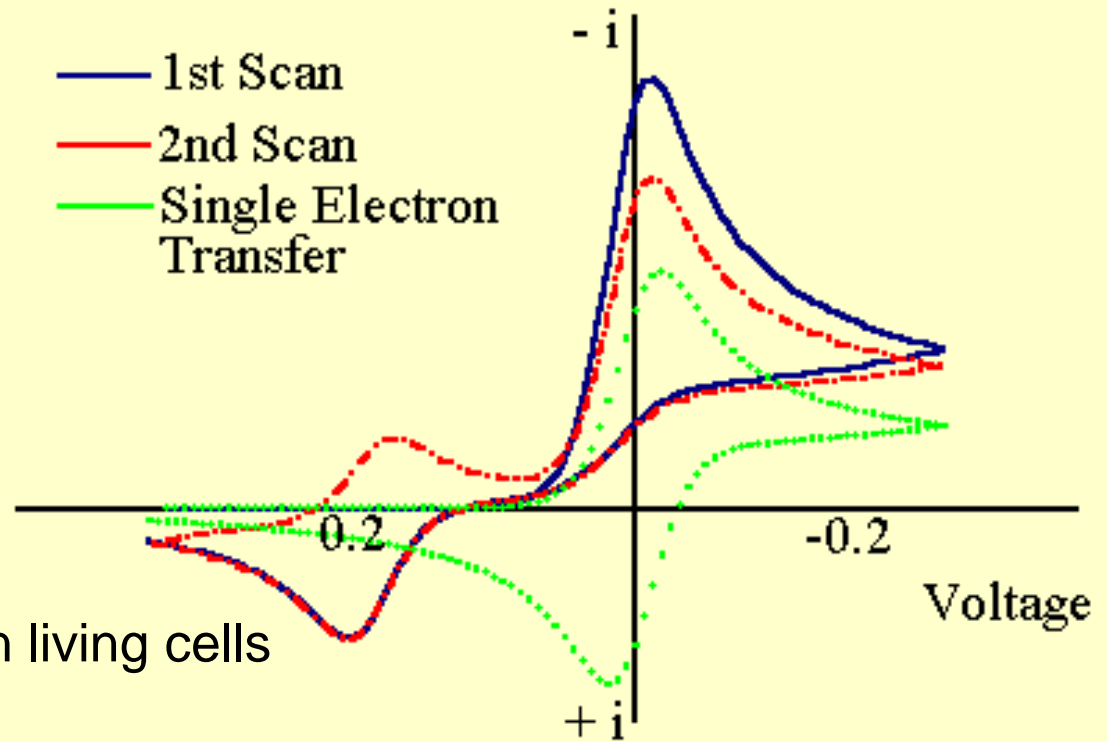
IN-VIVO voltammetric determination of catecholamine



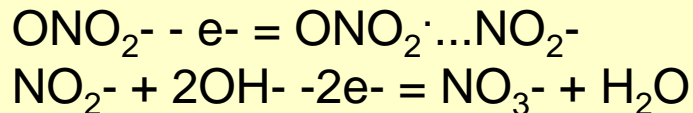
What kind of information can provide Voltammetry?

-Mechanism pathway

-detection of the **intermediates** and final products of the redox reactions



Peroxyde nitrite oxidation in living cells

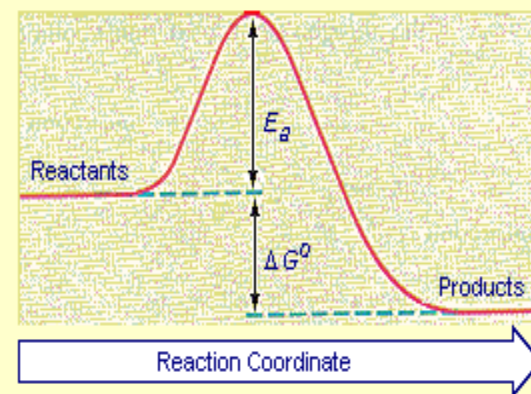
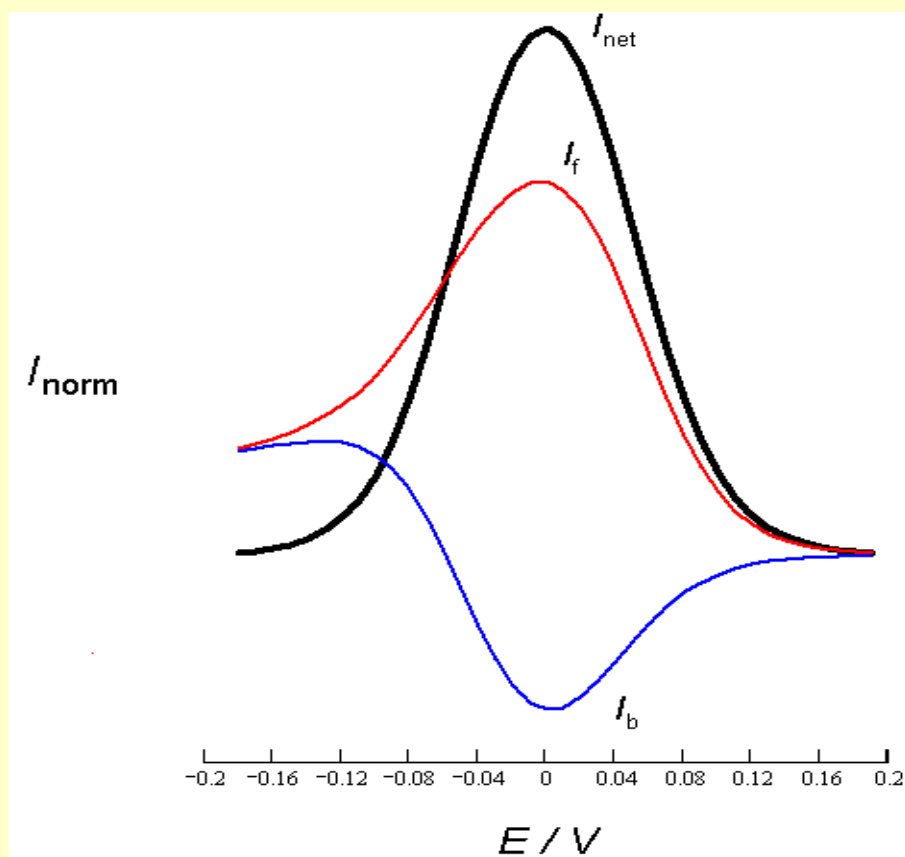


-Thermodynamic Parameters of Redox Reactions

Standard Redox Potential-Energy of Activation., Enthalpy, **Complexation Constants...**

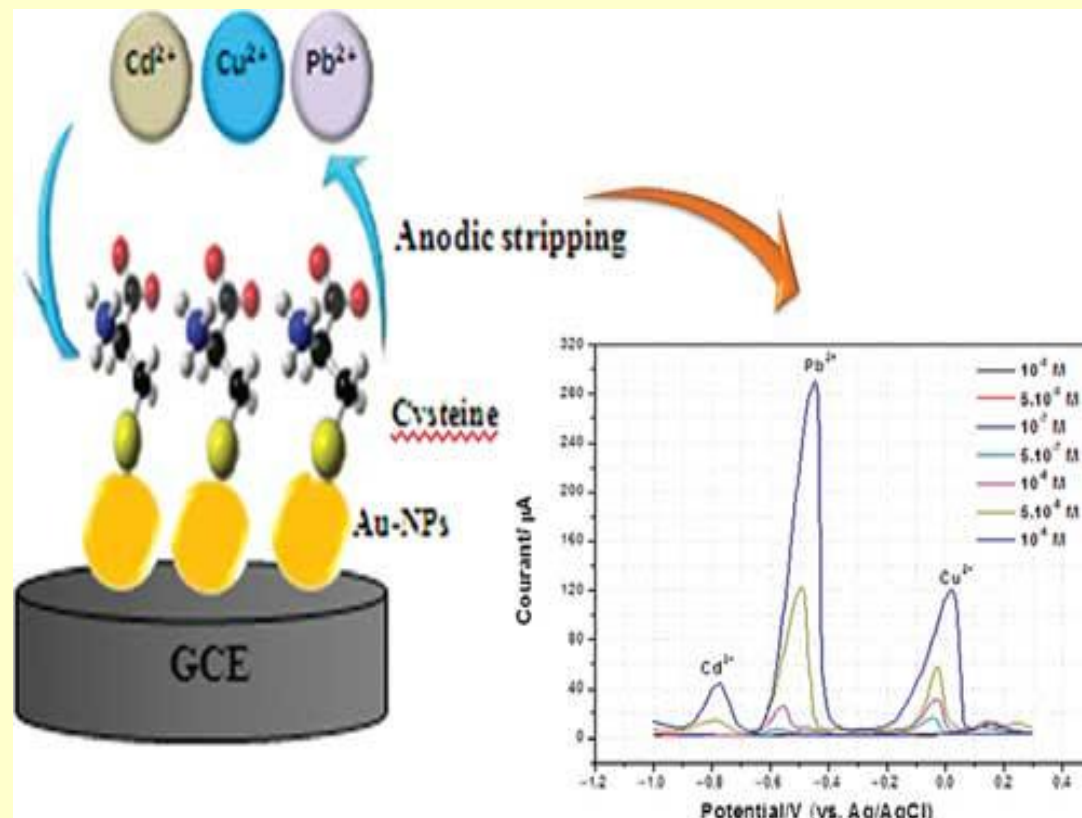
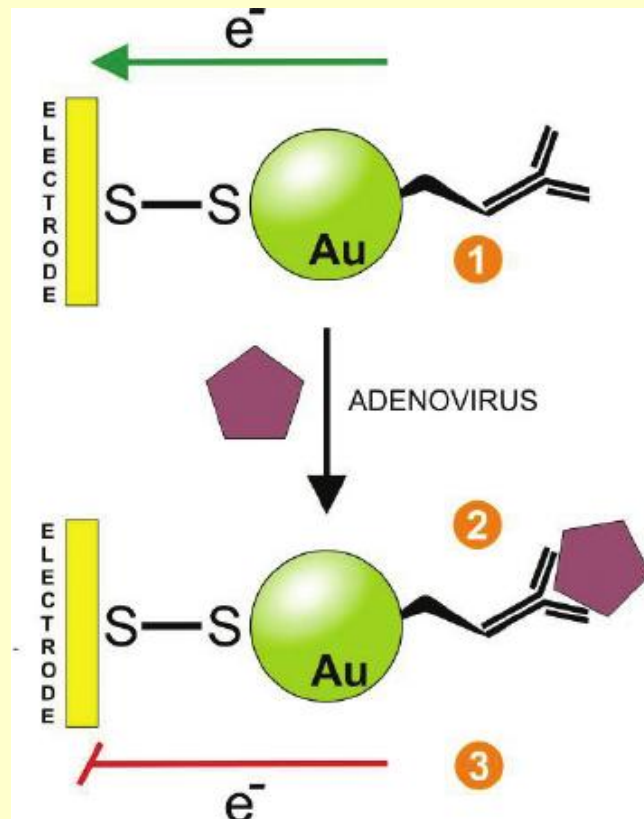
-Kinetic Parameters

-standard rate constants of electron/ion transfers; kinetics of enzymatic reactions; kinetics of chemical reactions; **pharmakokinetic parameters...**



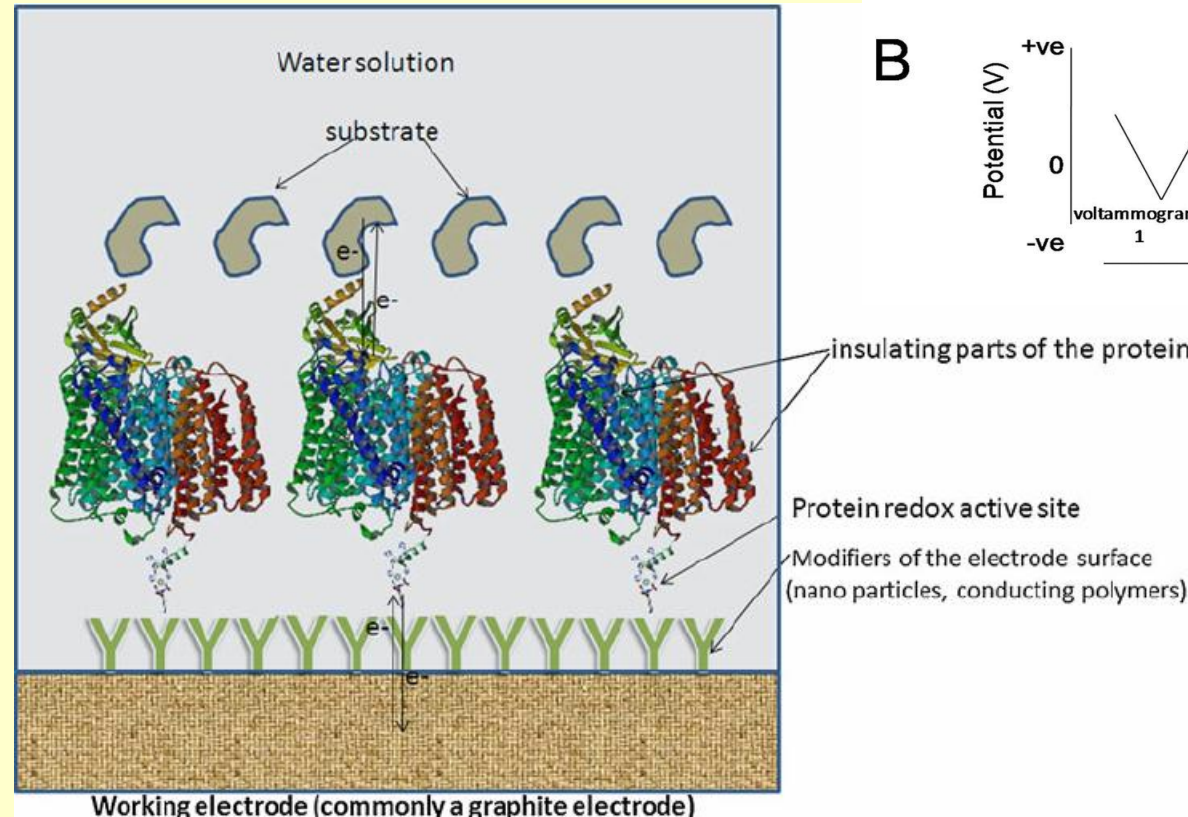
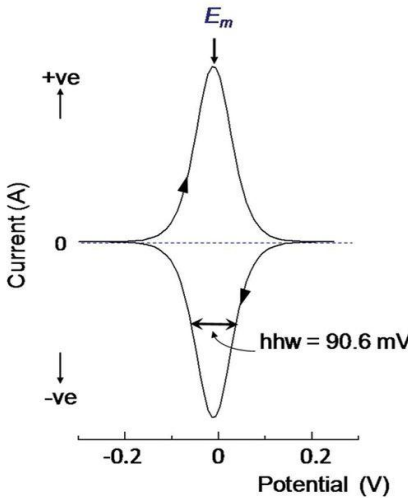
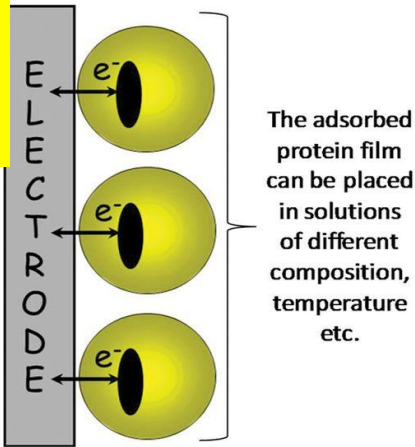
Voltammetry-NANOPARTICLES MODIFICATION

-new way of improving electrochemical signals-

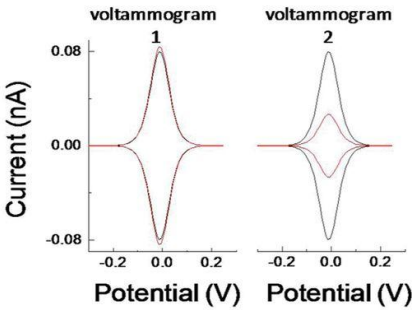
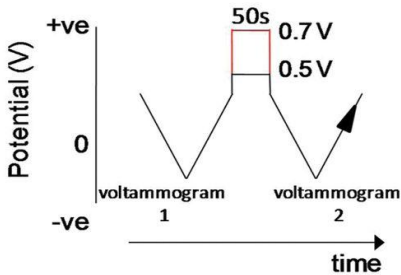


PROTEIN-FILM VOLTAMMETRY

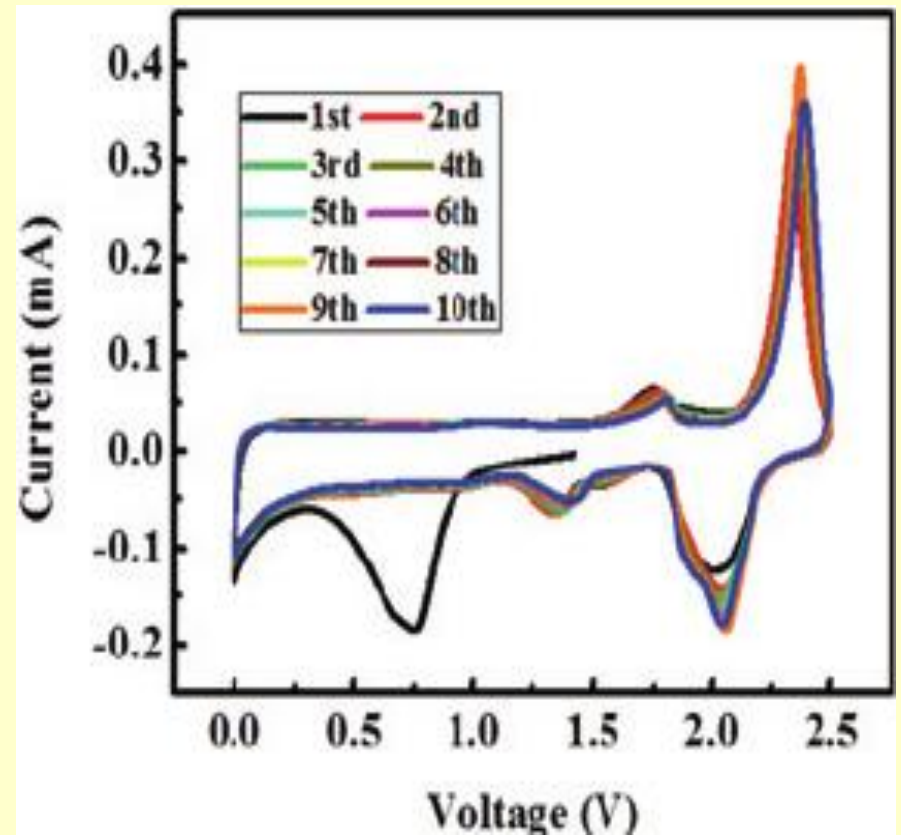
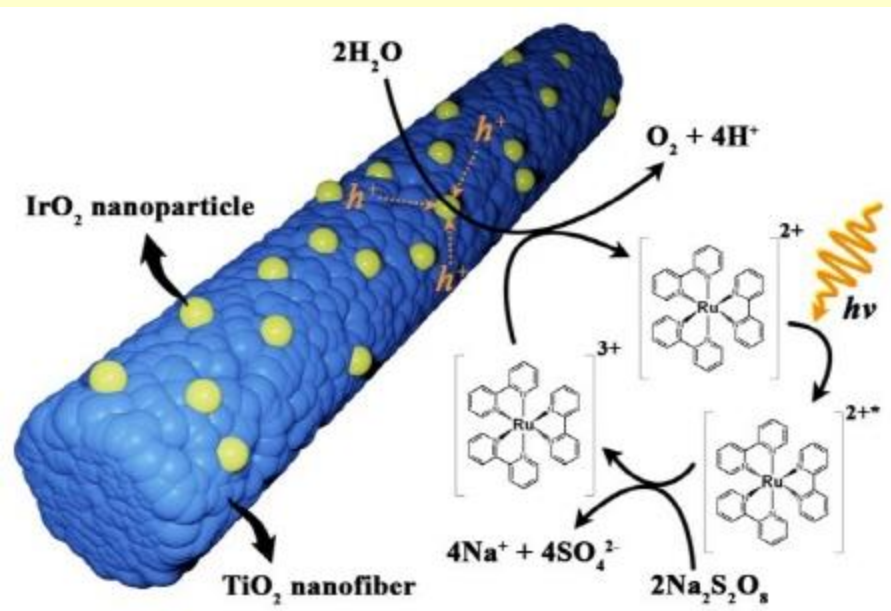
Enzymes-Redox Chemistry



B



Voltammetry of BIOMATERIALS



Voltammetry is a tool for Designing BIOSENSORS

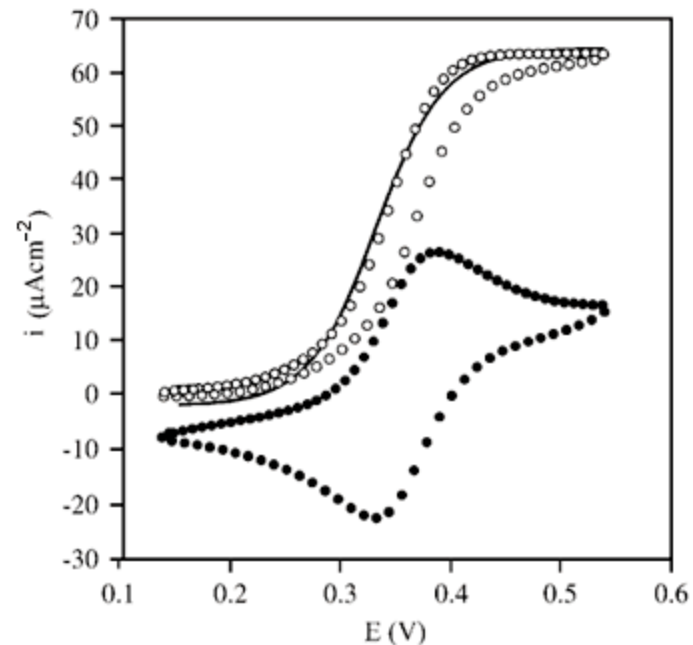
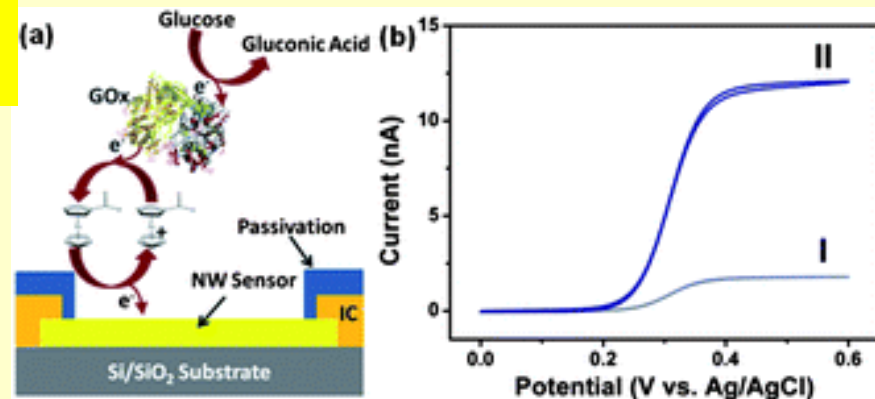
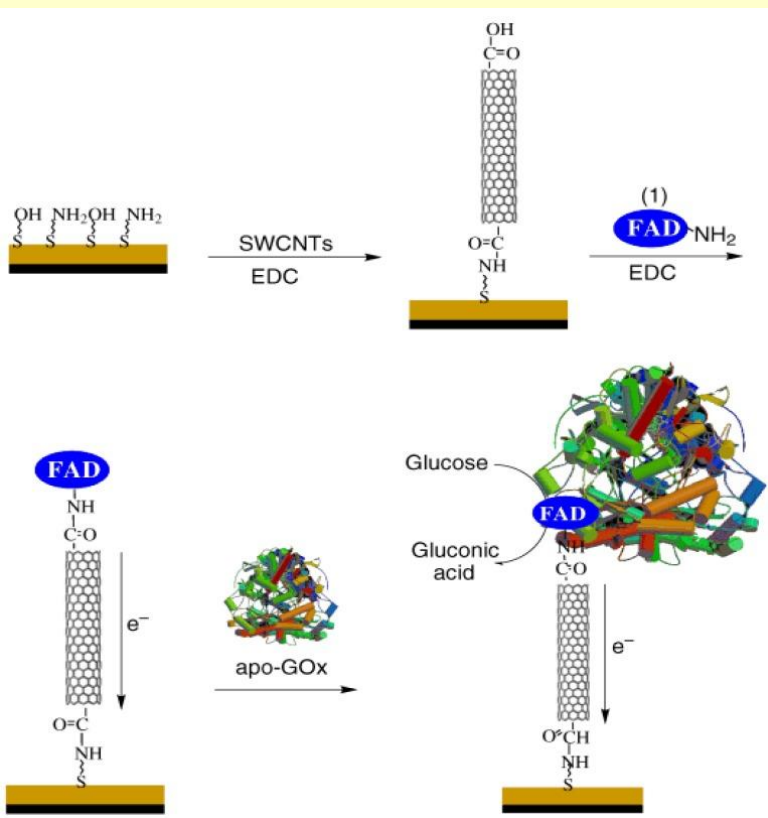
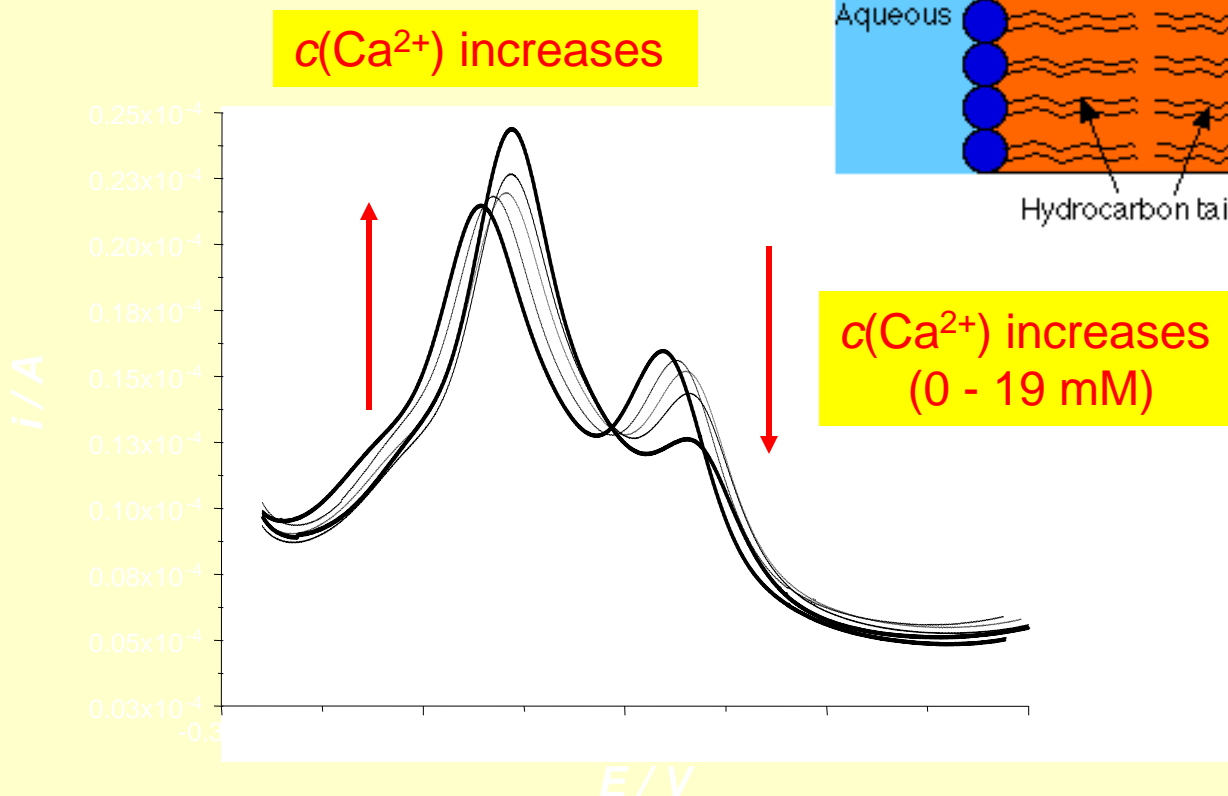
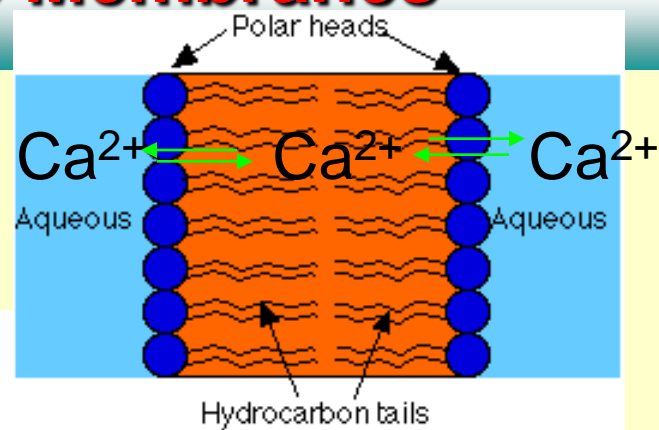


Figure 5. Catalytic wave for glucose oxidation in 50 mM phosphate buffer pH 7.1 and 0.1 M KNO₃ at a Fc-PAA-GOx hydrogel modified electrode (•) glucose free solution 10 mV s⁻¹ and (o) 0.1 M glucose solution 5 mV s⁻¹. Solid line corresponds to best fit to Eq. 8. (see text).

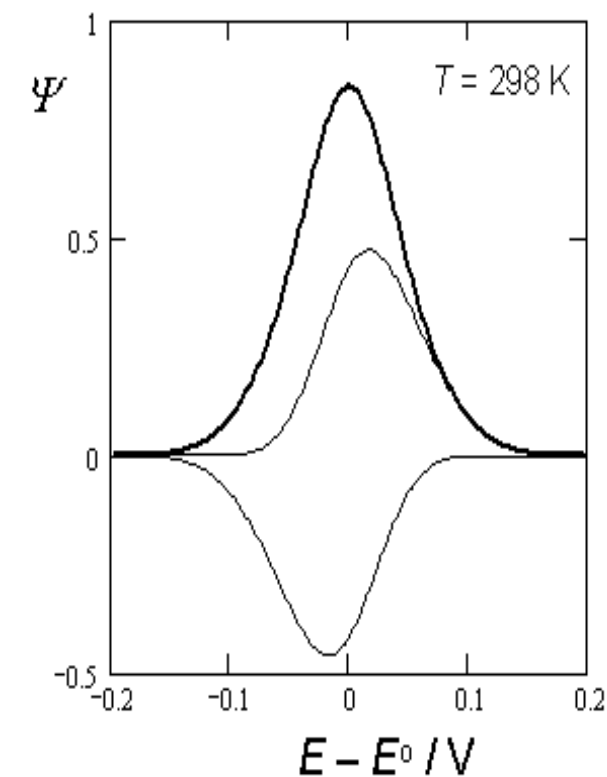
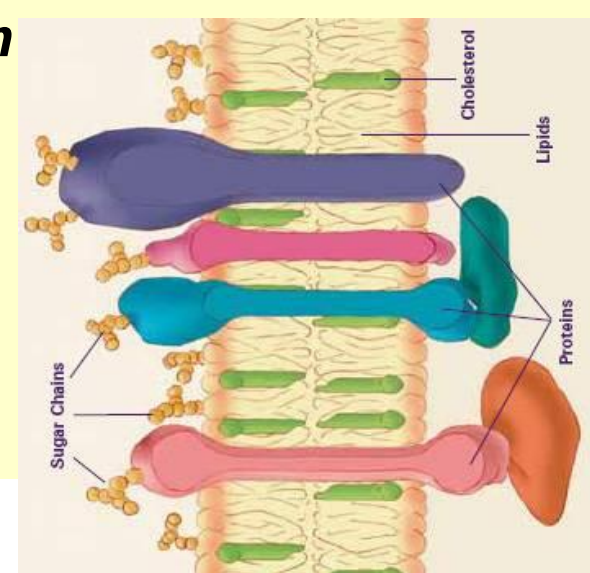
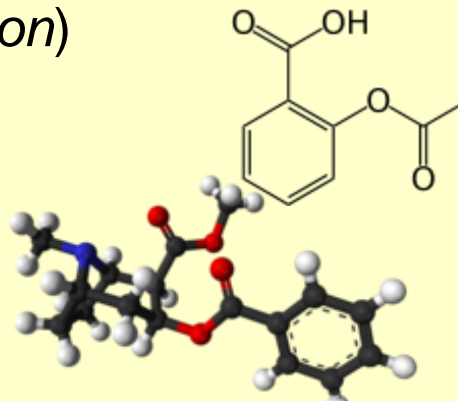
Transfer of Ions Across Membranes



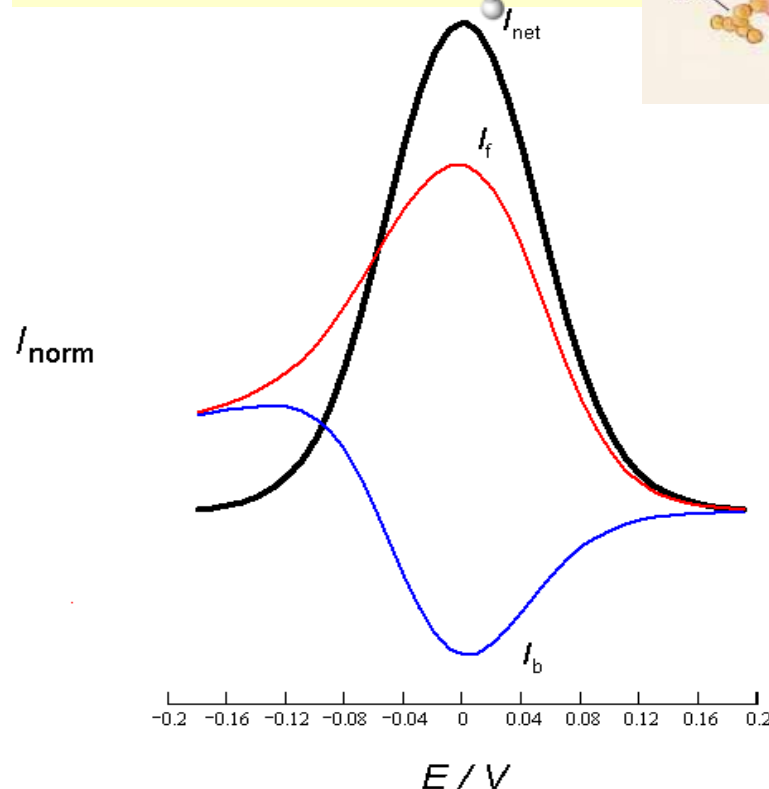
Cyclic voltammograms showing complexation of PalmytoilQuinone with Ca^{2+}

-physical phenomena taking place in the system
(absorption, phase transformation)

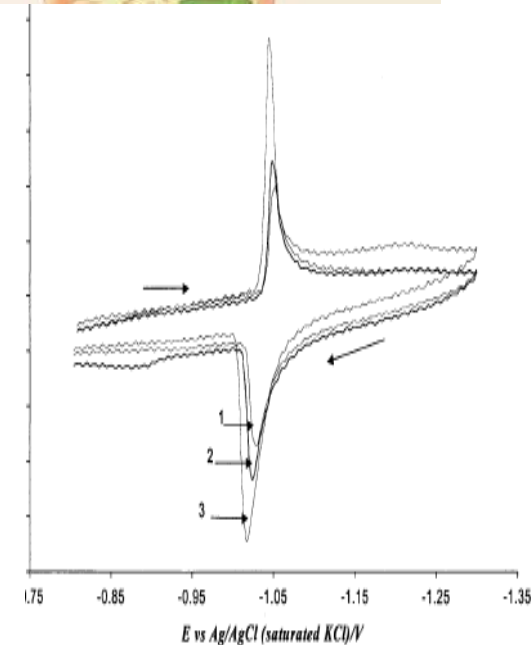
-way of mass transfer



absorption



diffusion

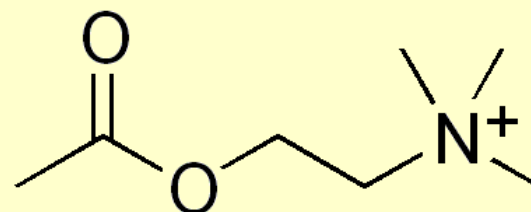
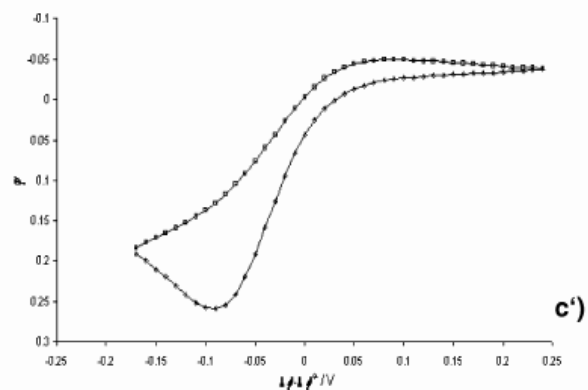
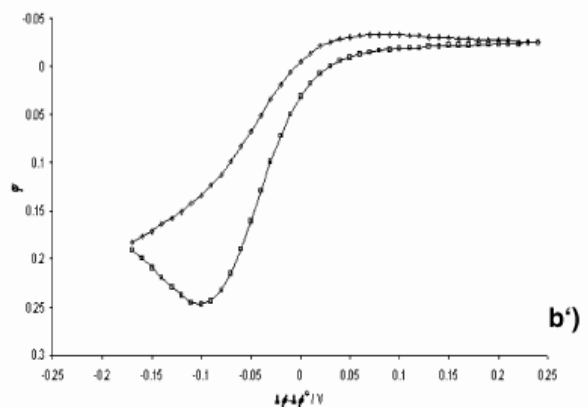
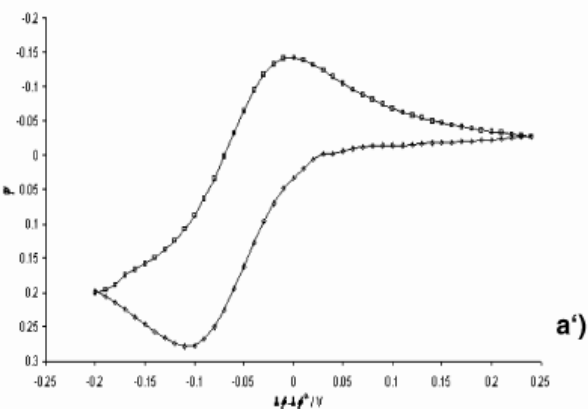


Phase-transformation

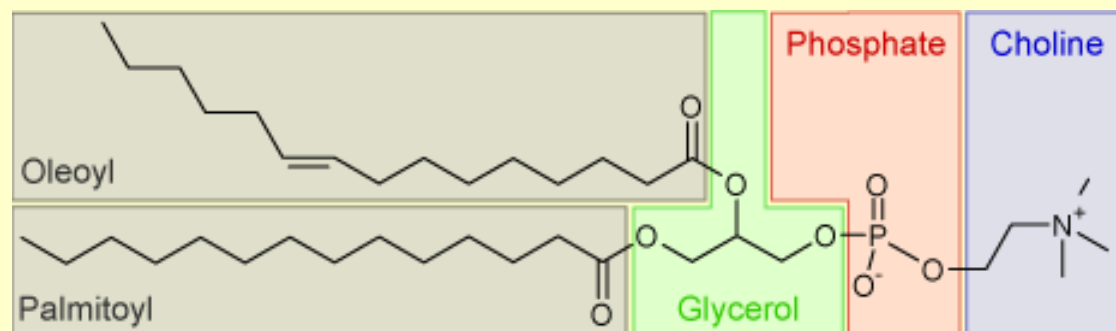
21

-thermodynamic and kinetic parameters related to the physical phenomena

-Strenghts of interactions between various substances



Acetylcholine



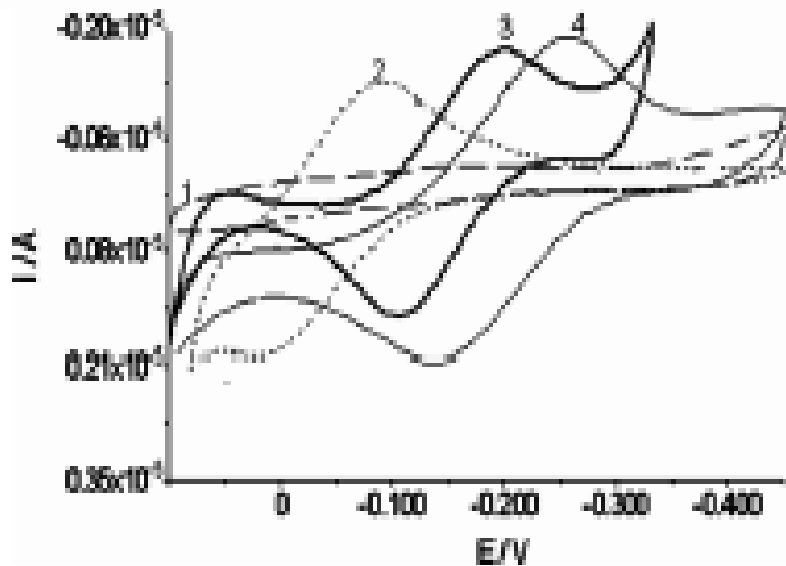
Phospholipids

TABLE 1: Determined Kinetic Parameters of the Ion Transfer of AcH^+ from Water to DCE (k_s and α) and for the Interactions between AcH^+ and DOPC (K , ϵ , k_f , and k_b)

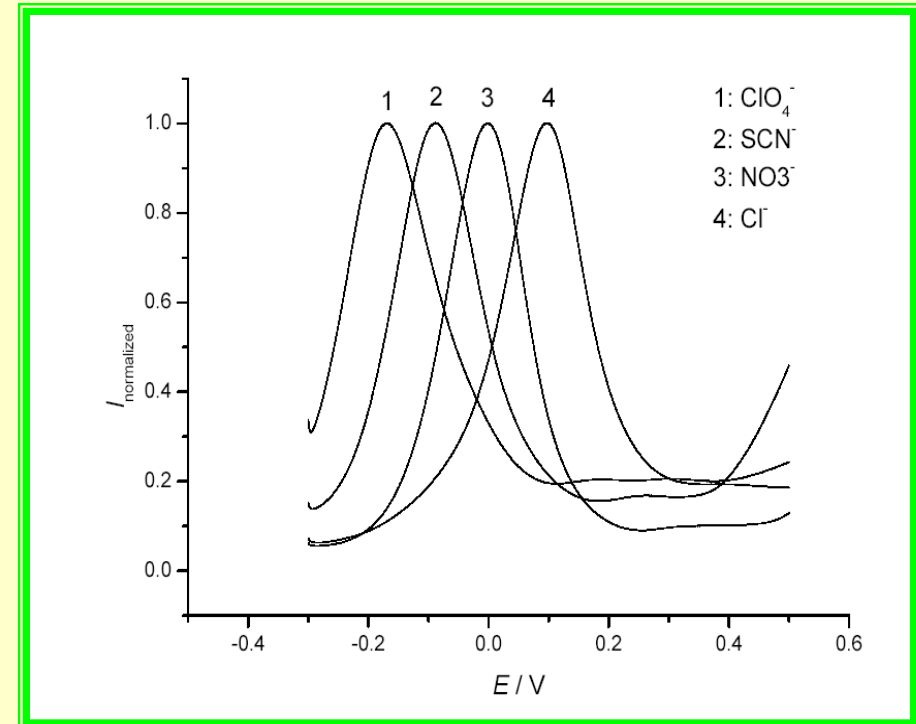
measuring technique	$k_s/\text{cm s}^{-1}$	α	K	ϵ/s^{-1}	k_f/s^{-1}	k_b/s^{-1}
SWV	0.0030	0.50	0.44	13.10	4.00	9.10
EIS	0.0033	0.53	0.80	13.30	5.90	7.40

Is it possible to investigate only the “electron” transfer reactions with Voltammetry?

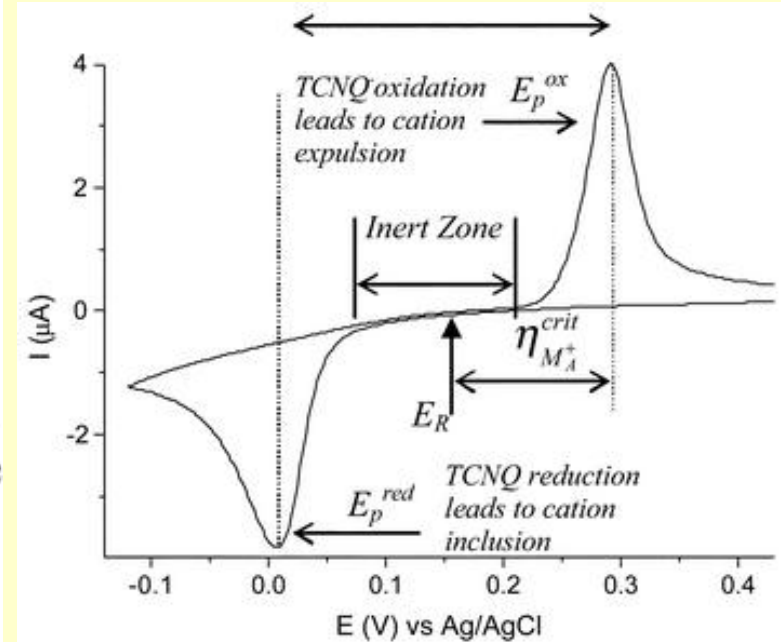
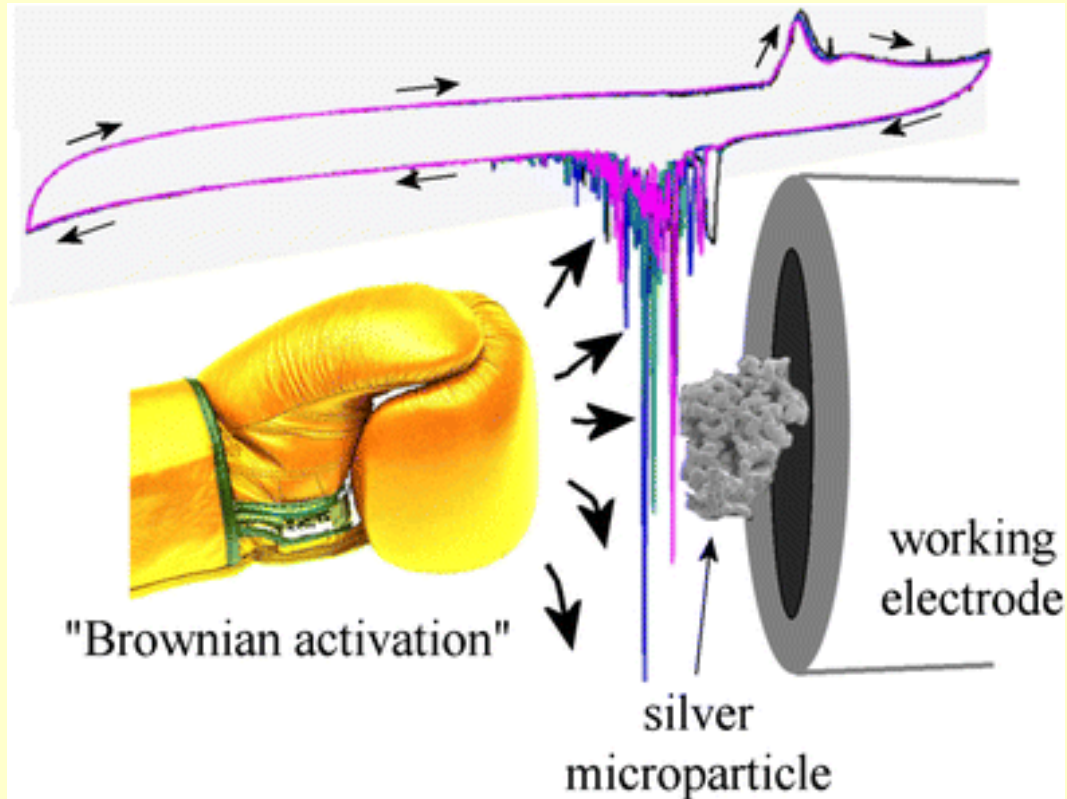
NO, it is possible to follow voltammetrically also reactions comprising only ION transfer, or COUPLED ELECTRON-ION transfer



Transfer of Ionized Drugs-
heroin, cocaine and codeine
across biomimetic membranes

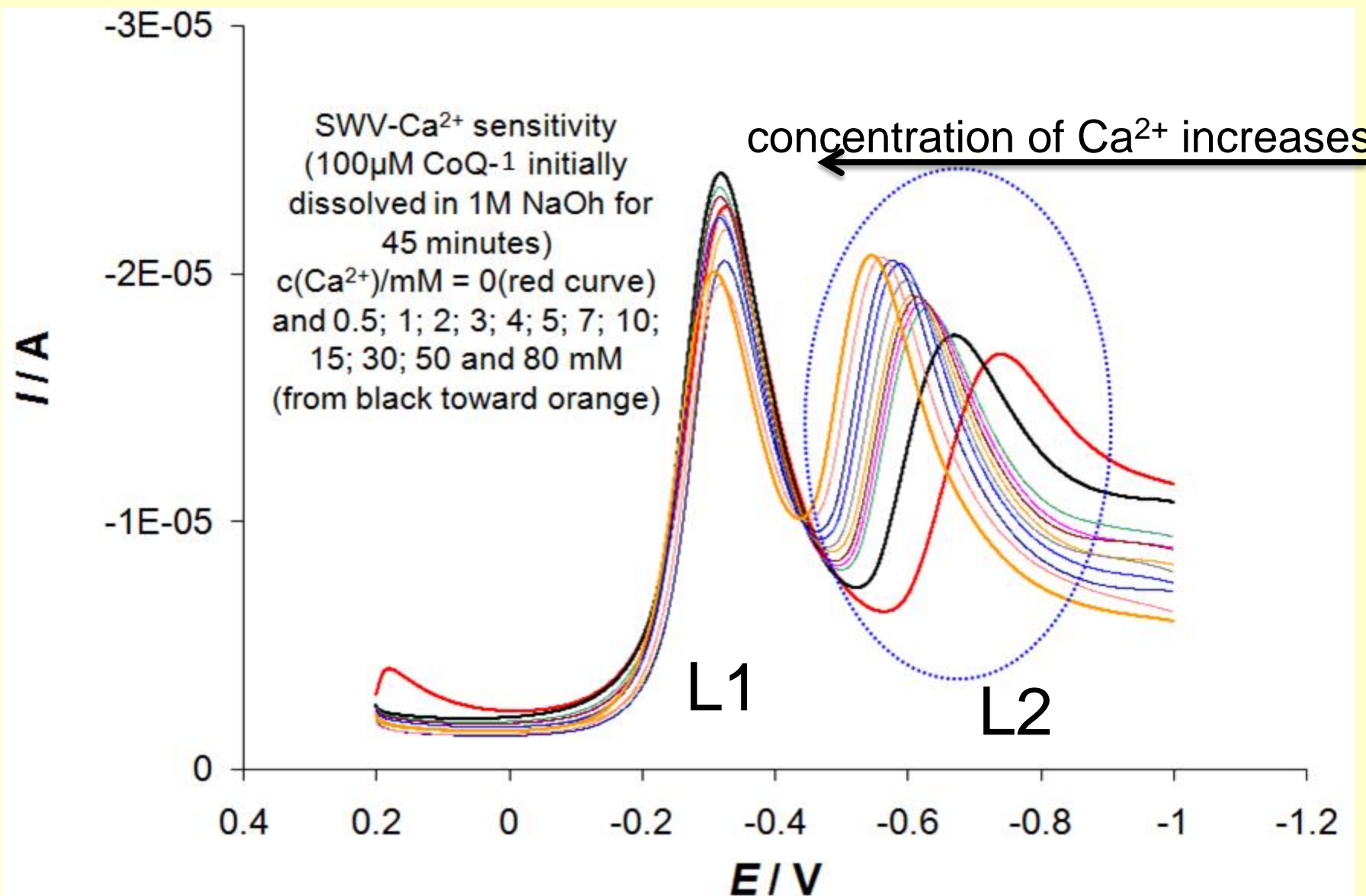


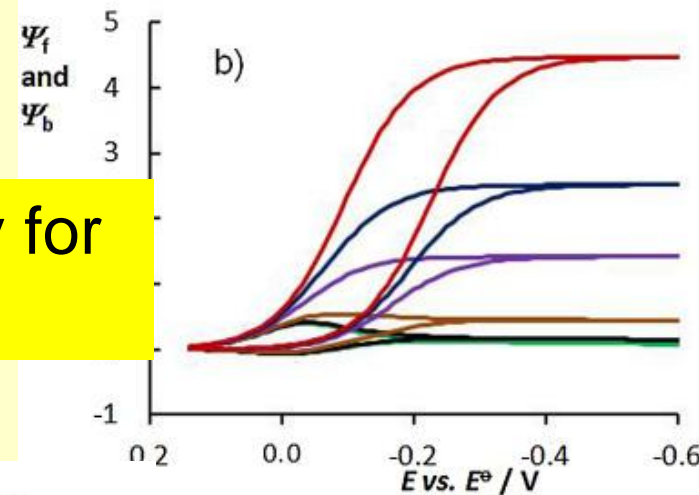
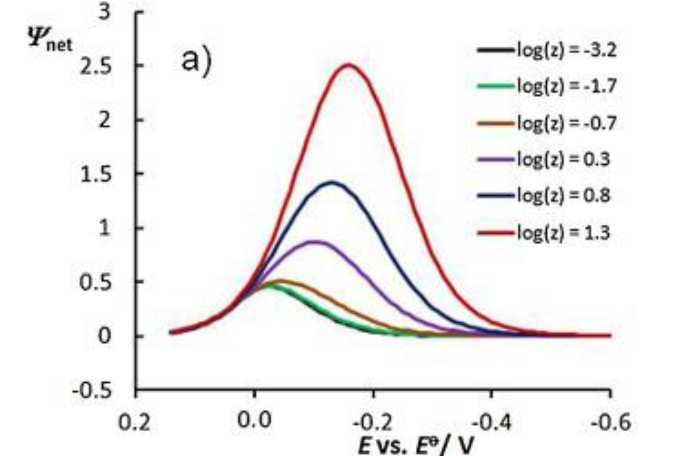
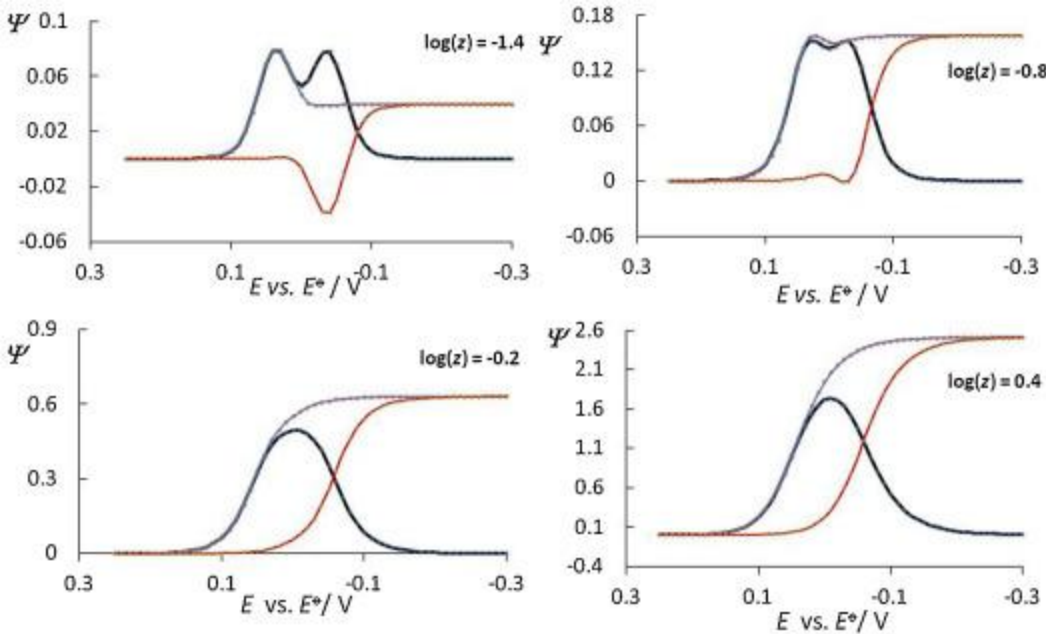
Voltammetry from Solid State



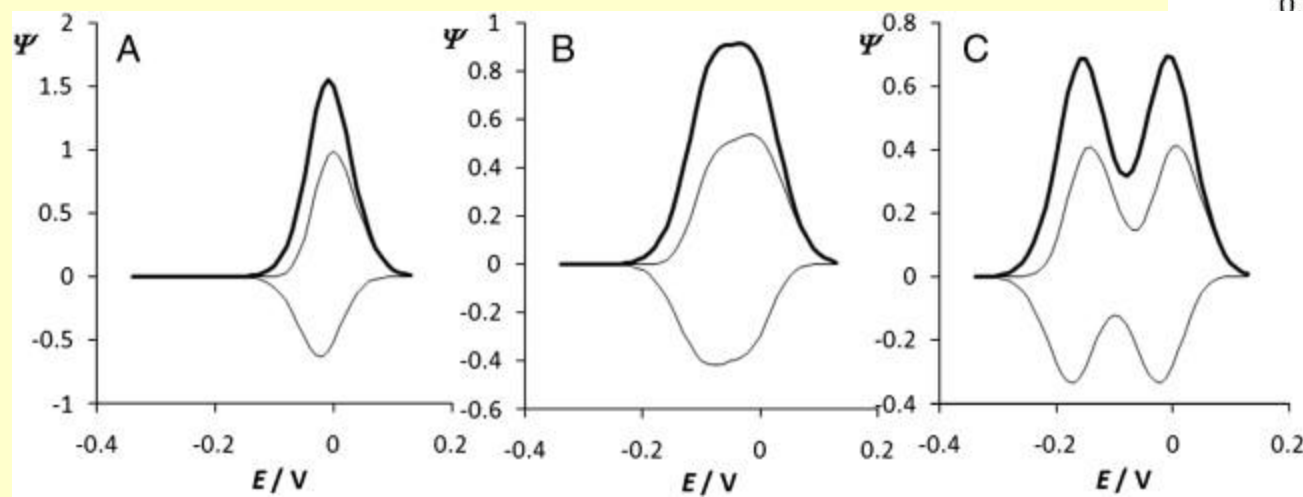
Pioneered by prof F Scholz

Complexation reactions.....





Well-Developed Theories in Voltammetry for Various Redox Mechanisms



Concluding remarks

...ADVANTAGES of using Voltammetry for characterization of biomaterials:

- fast instrumental technique
- extremely cheap instrumentation
- common chemicals are used available in every Lab
- ...suitable for qualitative, quantitative studies, Mechanistic studies, kinetic and thermodynamic measurements

Total costs for the voltammetric instrumentation

3-4000 Euros!!!!

**Amazing!!! ONE CAN MAKE GREAT SCIENCE WITH
Small AMOUNT OF MONEY!!!!**



EmStat is the smallest electrochemical interface available on the market. The EmStat series are general purpose potentiostats which are also highly suited for embedded use in applications.

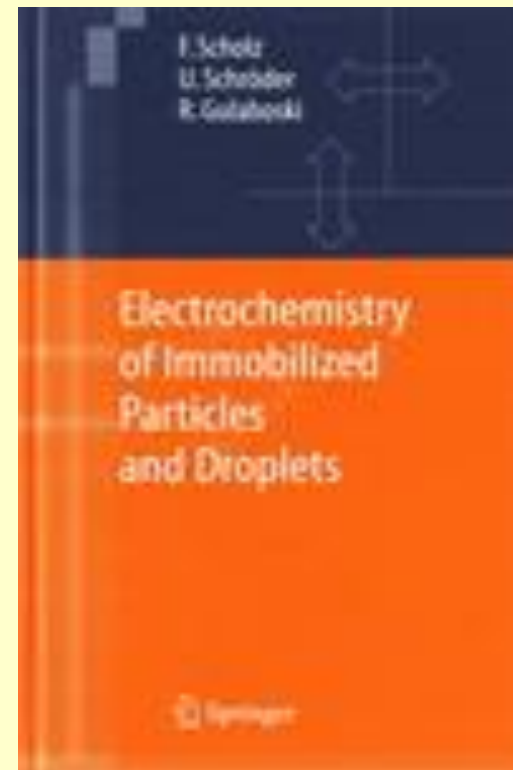
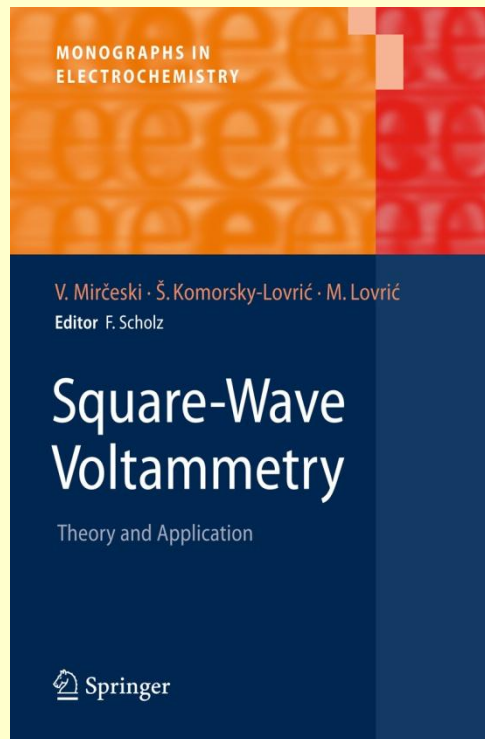
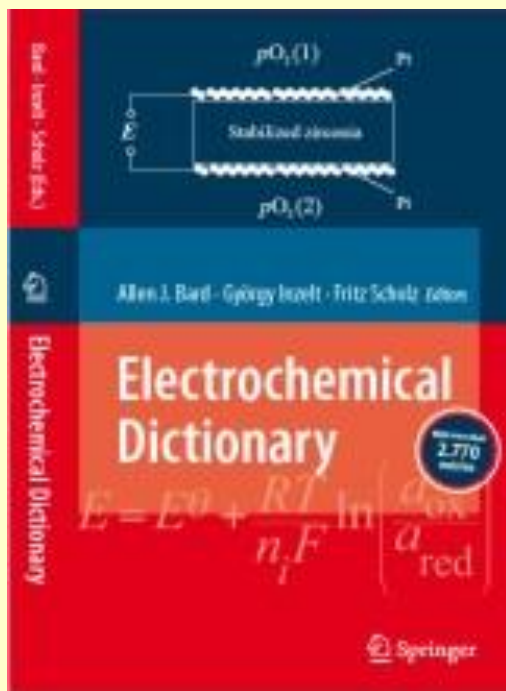




What did I lose?
and

What did I get

From AvH and DAAD



ELECTROCHEMICAL DICTIONARY (2008)

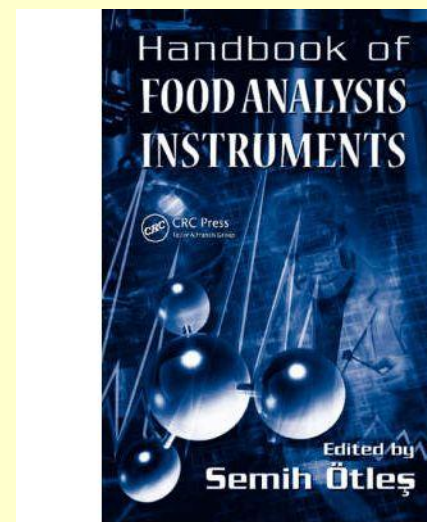
A. J. Bard, G. Inzelt, F. Scholz (editors)

F. Scholz, U. Schroeder, **R. Gulaboski**

R. Gulaboski, C. M. Pereira in

Handbook of Food Analysis Instruments (2008)

Semih Otles (Ed.)



But...this is the biggest POWER of Voltammetry



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Greifswald University



Prof. Valentin Mirceski
Macedonia University



Prof. Markus Hoth
Saarland University



Prof. Reinhard Kappl
Saarland University



Prof. Carlos Pereira
Porto University



Prof. Milivoj and Sebojka Lovric
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National:



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